

Occupational and Environmental Health Hazards in the Plastics Industry

by Robert E. Eckardt*

A brief description of the potential occupational health hazards encountered in the manufacture of plastics (polymers) is given. In general, these hazards are due to the monomers used to make the various plastics, to unreacted monomer contained within the finished products, and to the fillers, stabilizers, pigments, inhibitors, and initiators used in fabricating the finished products. They run the gamut from angiosarcomas of the liver due to vinyl chloride, to dermatitis and asthma-like reactions due to the initiators used with epoxy resins.

It is impossible, in the time allotted today, to describe for you in any detail all of the occupational and environmental health hazards of plastics. At best, all we can hope to do is outline some of the more obvious ones in a general way. I have previously reviewed this topic in more detail (1).

We might start by defining a plastic as "a material that contains as an essential ingredient an organic substance of large molecular weight, is solid in its finished state, and, at some stage in its manufacture or in its processing into finished articles, can be shaped by flow" (2). In many cases, the terms plastic and resin are used in an overlapping sense. However, strictly speaking, a resin is the more or less homogeneous polymer used as the starting material in the production of a molded article, while plastic signifies the finished product which may contain fillers, plasticizers, stabilizers, pigments, etc.

In general, the principal hazards of plastics are associated with their monomers and with the plasticizers, stabilizers, "activators," fillers, and pigments that are used in them. Although there are exceptions to this, this statement generally holds true.

Of course, the hazard we are all most acutely aware of today is that of liver angiosarcoma

and acroosteolysis production from vinyl chloride. The discovery of these two quite different, and apparently distinct, clinical entities in both humans and animals came as a rude shock to industry, government, and the medical profession. The suggestion, again from both animal experiments and epidemiological studies, that other types of tumors may result from vinyl chloride exposures is still being actively investigated. In many ways, these observations with vinyl chloride may have been a good thing, because this compound, long thought to be a relatively nontoxic material and even considered for use at one time as a general anesthetic in humans, has served to alert all of us—those in industry, government, and academia—to the rather meager toxicologic knowledge we have of many commodity chemicals that are used widely in great volume. One of the questions I hear raised very frequently among my associates in the chemical industry is "What will be the next vinyl chloride?" One good result has been the formation by 17 chemical companies of the Chemical Industry Institute of Toxicology (CIIT) under the leadership of Dr. Leon Golberg. The avowed intent of this institute is to study in depth and in a systematic fashion the toxicology of high volume commodity chemicals. Their budget will gradually increase from a level of about \$1.5 million per year to a level of \$5 million annually, or pos-

* Exxon Corporation, P.O. Box 45, Linden, New Jersey 07036.

sibly even more if this seems warranted from their initial experiences.

Two further nagging questions have to be pursued until a definitive answer has been reached. The first of these is the suggestion by Infante (3) of NIOSH that vinyl chloride may be causing an increased incidence of teratogenic effects in towns which have PVC plants. Because many medications, including salicylates, and infections (4) can lead to teratogenic effects, more careful analysis of these data needs to be undertaken, to exclude the influence of these other factors. Second, television channel 5 in New York has recently suggested in its evening news broadcasts that PVC used as insulation on electrical wiring in high-rise apartments may represent an increased risk due to the evolution of hydrochloric acid in the event of a fire in such buildings. This situation needs careful comparative examination with the potential risks of the combustion products of other types of electrical wire insulation materials. That hydrogen chloride is evolved during the incineration of PVC was demonstrated by the EPA several years ago in garbage incinerators.

The oldest synthetic plastic is celluloid, a cellulose nitrate. Its principal occupational hazard arose from the nitric acid used in its manufacture, a well-recognized industrial hazard. Its principal environmental hazard was its flammability, and many serious injuries and deaths resulted from this cause among users of celluloid collars and cuffs. The x-ray films in the famous (or infamous) Cleveland Clinic fire were made of cellulose nitrate and evolved much nitrogen oxides during the fire, which led to many immediate and delayed deaths.

Bakelite, a condensation product of phenol and formaldehyde, was one of the next commercial plastics. Its components, phenol and formaldehyde, are both well-recognized industrial toxic materials which have to be handled with caution.

Cellulose acetate replaced cellulose nitrate for use in photographic film and considerably reduced the flammability hazard and the hazard of nitrogen oxides evolution in a fire.

Urea-formaldehyde resins came into use in 1929, and again the toxic properties of the ingredients were pretty well understood. Urea has been shown to be an irritant to the lung but is otherwise considered nontoxic because it is a

natural metabolite of protein. Formaldehyde is a well known mucous membrane irritant and a cause of dermatitis in those who become sensitized to it.

Polyvinyl esters, which include poly(vinyl acetate), poly(vinyl chloride), copolymers of vinyl chloride and vinyl acetate, and poly(vinyl acetals), came into use about the same time as urea-formaldehyde resins. Interestingly enough, vinyl acetate does not seem to have the same toxic and carcinogenic properties as vinyl chloride (5).

When a high purity styrene could be produced in 1937, this led to the introduction of polystyrene. Styrene is not at the present time believed to be a particularly toxic material but it is undergoing intensive toxicological testing at the present time by a task force of the Manufacturing Chemists Association.

Cellulose acetate butyrate replaced cellulose acetate in photographic and other films with no accompanying change in hazard.

Nylons are basically polyamides, with different grades being made by different processes. Nylon 66 is a condensation product of adipic acid and hexamethylenediamine. The hexamethylenediamine is a skin and eye irritant and skin sensitizer, and therefore, has to be handled with adequate precautions in the occupational setting. When nylon stockings were first introduced, there were many reported cases of skin reactions, at first believed due to the nylon itself. Extensive studies by the DuPont Company established that most, if not all of these, were due to the sizing and dyes rather than to the nylon itself. Nylon 6 is a polymerization product of caprolactam. Caprolactam is an irritant to skin and mucous membranes and has to be used in the occupational setting with adequate protection.

Melamine-formaldehyde resins came into use in the late 1930's and are extensively used in tableware. The problems of formaldehyde are well known, and melamine has been shown to have a low order of toxicity.

Cellophane, interestingly enough, is a reconstituted cellulose that could be described as a form of rayon. Its principal occupational hazard is from carbon disulfide used as a solvent in the manufacturing process. The toxic properties of carbon disulfide have been under study for a number of years. It is an acutely toxic material with reactions similar to those pro-

duced by hydrogen sulfide. Chronically, it can produce a whole host of symptoms, terminating in chronic dementia if exposure is long enough to a sufficiently high level. Although the presently accepted TLV for carbon disulfide is 20 ppm, it is likely that this level is too high and further reductions will need to be accomplished.

Silicones are organosiloxane polymers which can be made in a variety of forms from liquids to solids, depending on the molecular weight. They have found a large variety of uses, even including breast enlargement, a practice recommended only with caution and careful medical supervision, if at all. They are very non-toxic materials and should present no occupational or environmental problems.

Polyethylene and polypropylene and ethylene-propylene copolymers are made from the indicated hydrocarbons ethylene and propylene. These hydrocarbons, particularly ethylene, are said to be simple asphyxiants and, therefore, to constitute no hazard to humans. However, several plants are known to exhibit an exquisite sensitivity to ethylene, suffering severe damage from exposure to very low concentrations. For this reason complete containment of ethylene is necessary to avoid plant damage. Additionally, in one process for making linear polyethylene, a "controlled explosion" constitutes the process. In this process, the ethylene is subject to very high pressure (5000 psi), from which it is suddenly released in the presence of a peroxide catalyst. Since these peroxide catalysts are themselves explosive, they have to be stored and handled in a special manner. In the plant that I visited, the reactor area is surrounded by 5-ft thick concrete shielding and direct access to the reactor area is not possible. The catalysts are stored behind an earthen bunker and handled by mechanical systems. It is evident that the hazards of this process have been carefully reviewed and a special design developed to contain them.

A variety of dermatitises and acute and chronic pulmonary problems have been associated with the use of two plastics, namely epoxides and polyurethanes, especially polyurethane foams. In the case of epoxy resins, these effects have been associated with the curing agents, namely ethylenediamine, diethylenetriamine and triethylenetetramine. These are highly alkaline compounds capable of causing extensive corrosive skin reactions. They

also are known skin sensitizers, and hence may cause allergic skin reactions. Because the reaction is exothermal, fumes may be produced which in sensitized individuals can lead to bronchial asthma. Since the curing agents may be used in excess, in order to drive the polymerization to completion, subsequent grinding, sanding, or polishing of epoxy resins may produce dusts and fumes, with all of the above-described reactions occurring. It is essential, therefore, that epoxy resins, either during the curing process or when undergoing subsequent finishing, be used with adequate ventilation, and/or adequate protective equipment such as gloves, masks, and protective goggles.

In the case of polyurethanes, toluene diisocyanate (TDI) or *p,p*-diphenylmethane diisocyanate (MDI) are used as catalysts and these can cause both acute and chronic pulmonary reactions. Bronchial asthma often develops in these workers. Peters (6) and others have shown that chronic impairment of pulmonary function in industrial workers may well result. If unreacted TDI or MDI remains in the product, this hazard can present itself to subsequent users of the polyurethane foam.

Polytetrafluorethylene (Teflon) has come into extensive use because of its extreme unreactivity. However, if it is ground or sanded, a fine dust can be produced which produces a polymer fume fever quite similar to metal fume fever. Care has to be exercised that workers do not carry cigarettes where they can be contaminated with this fine dust, because subsequent smoking of such contaminated cigarettes can lead to serious consequences in the smoker. Although this is well-recognized in industry, it is not so clear that home users of Teflon products are aware of this potential hazard.

Acrylic resins are polymers of acrylic acid, methacrylic acid, esters of these acids, or acrylonitrile, of which Lucite is a good example, and are widely used, especially in the preparation of dentures. These monomers may be severe skin and eye irritants, and acrylonitrile has many of the toxic properties of the cyanide ion. They must be used with adequate precautions in industry.

As previously stated, most of the plastics we have discussed thus far are relatively physiologically inert. However, should they contain unreacted monomer, they could then exhibit the toxic properties of the monomer. Thus,

formaldehyde-containing plastics could produce dermatitis if some unreacted formaldehyde is present. Skin and eye irritation could result from unreacted acrylic monomers, and we have already discussed skin and pulmonary reactions from unreacted amines or isocyanates. When subjected to thermal breakdown, as in fires, many of these polymers will produce a whole host of toxic breakdown products, such as HCl from PVC, aldehydes from many of them, and HCN from acrylonitrile-derived polymers. It is beyond the scope of this paper to discuss these thermal breakdown products in detail.

Since a great variety of fillers, pigments, stabilizers, inhibitors, etc. are used in finished products, a detailed discussion of these is also beyond the scope of this paper. Glass, wood dust, asbestos, and cadmium or chromium salts, may all be used in such applications. Obviously the occupational or environmental health hazard implications of such materials would be dependent upon the inherent toxicity of each.

One further potential hazard needs to be mentioned, if only in passing. Many of these plastics, when implanted in sheet or pellet form in the subcutaneous tissue of animals, will produce local sarcomas. If perforated sheets or powdered plastic is used, these sarcomas do not appear. This information should be care-

fully evaluated; perhaps, additional tests should be run if plastics are being considered for implantation at any site in the human body. The nature and extractibility of fillers, pigments, stabilizers, and inhibitors should also be given due consideration before a plastic is used in medical applications, such as tubings, syringes, containers, etc. The possible implications of phthalate plasticizers used in medical applications was the subject of a whole conference held at Pinehurst, North Carolina, about a year ago.

REFERENCES

1. Eckardt, R. E., and Hindin, R. The health hazards of plastics. *J. Occup. Med.* 15: 808 (1973).
2. Rose, A., and Rose, E. Ed. *The Condensed Chemical Dictionary*, 6th ed., Reinhold, New York, 1961.
3. Infante, P. F. Oncogenic and mutagenic risks in communities with polyvinyl chloride production facilities. In: *Occupational Carcinogenesis*, V. Saffiati and J. K. Wagoner, Eds., N. Y. Academy of Sciences, New York, 1976, p. 49.
4. International Conference on Birth Defects: Detection and Prevention. Sponsorship by the Institut de la Vie (Paris), Martinique, January 26-28, 1976.
5. Maltoni, C., and Lefemine, G. Carcinogenicity bioassays of vinyl chloride. I. Research plan and early results. *Environ. Res.* 7: 387 (1974).
6. Peters, J. M., and Wegman, D. H. Epidemiology of toluene diisocyanate (TDI)-induced respiratory disease, *Environ. Health Perspect.* 11:97 (1975).